(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 677 572 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **95105672.0**

(22) Date of filing: **13.04.95**

(51) Int. Cl.[6]: **C10M 159/12**, C10M 133/52, C10M 177/00, //C10N40:25, C10N30:04,C10N30:02

(30) Priority: **15.04.94 HU 1100094**

(43) Date of publication of application: **18.10.95 Bulletin 95/42**

(84) Designated Contracting States: **AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE**

(71) Applicant: **MOL MAGYAR OLAJ ES GAZIPARI RESZVENYTARSASAG**
18 Oktober 23 u.
H-1051 Budapest (HU)
Applicant: **VESZPREMI EGYETEM**
Egyetem ut 10
H-8201 Veszprém (HU)

(72) Inventor: **Dénes, Ferenc Dr.**
10 Kis. u.
H-2921 Komárom (HU)
Inventor: **Kis, János**
23 Fö u.
H-2931 Almásfüzitö (HU)
Inventor: **Baladincz, Jenö**
10 Báthory u.
H-2900 Komárom (HU)
Inventor: **Auer, János**
19 Pipacs u.
H-2903 Komárom (HU)
Inventor: **Deák, Gyula Dr.**
23 Bethlen u.
H-4400 Nyiregyháza (HU)
Inventor: **Bartha, Laszlo Dr.**
3 Billege u.
H-8200 Veszprém (HU)
Inventor: **Hancsok, Jenö Dr.**
25/B Egry J.u.
H-8200 Veszprém (HU)
Inventor: **Kovács, Magda Dr.**
16/C Diofa u.
H-8200 Veszprém (HU)

(74) Representative: **von Füner, Alexander, Dr. et al**
Patentanwälte v. Füner, Ebbinghaus, Finck
Mariahilfplatz 2 & 3
D-81541 München (DE)

(54) Detergent-dipersant additive for lubricating oils of internal combustion engines and its preparation process.

(57) An additive for lubricating oils of internal combustion engines containing the imide- and/or ester and/or ester-amide, derivatives of the reaction product of an unsaturated polyisobutylene and some unsaturated reactive dicarboxylic acids and/or their anhydride comprising the reaction product of a polyisobutylene of a number average molecular weight 800 - 30 000 and an unsaturated reactive dicarboxylic acid and/or its anhydride, preferably maleic anhydride containing 1.6 - 6.0 SA - derivative per polyisobutylene chain on the average having a concentration of molecules containing more than one SA - derivative more than 25 weight percent and the polyisobutylene is grafted or reacted with an SA containing copolymer formed from a more reactive, low molecular weight comonomer of a molecular weight less than 500, containing olefinic double bond or from a mixture of such comonomers and from unsaturated reactive dicarboxylic acid and/or their anhydride, preferably maleic anhydride using the molar ratio 1.2 - 5.5 : 0.1 - 3.5 : 1 = MAH : comonomer : polyisobutylene, and in which the widening of the molecular weight distribution is less than 70 percent, referred to the starting polyisobutylene, while the SA groups of the copolymer linked to the polyisobutylene are reacted, in a 0.7 - 5.5 ratio, with compound containing at least bifunctional amine and/or hydroxyl groups. The invention disclosed the process of preparation of the additive.

EP 0 677 572 A2

The subject of the present invention relates to a grafted polyolefin - polysuccinic anhydride based ashless detergent dispersant (DD) additive that increases both viscosity and viscosity index and which can be used advantageously for improving the properties of lubricating oils and to the manufacturing process thereof.

The ashless, imide and ester type additives synthesised from alkenyl-succinic acid derivatives have been used for more than thirty years for the improvement of the detergent - dispersant properties of motor oils. Due to their polar and often basic character these additives restrict the formation and surface deposition of the insoluble acidic contaminations developed during the operation of the engine. Thus the life span of the engine and the duration of applicability of oils are thereby significantly increased.

The various, so called, modified derivatives containing sulfur, boron, halogens, molybdenum, copper atoms etc. exhibit good anticorrosion and antiwear properties beside their DD effect, whereas those containing large molecular weight ($\overline{M}_n$ > 2000) polymer side chains impart viscosity and viscosity index improving properties.

The alkenyl-succinic acid derivatives are generally mixed into the lubricating oils together with other metal containing DD additives, with VI improvers, antioxidants, anticorrosion and antiwear components, friction modifiers and foam inhibitors making use of advantageous interactions.

In the last ten years, the manufacturers of oil additives directed their research to improve the DD efficiency and the advantageous by-effects. According to results of engine tests this can be achieved either by increasing the molecular weight of the intermediates and the end product, or by the formation of polysuccinimides, polyesters, polyester-amides etc. coupled through their polar groups (e.g. U.S. Patent No.4.234,435).

The synthesis of such additives is based on the recognition that in the first step of the succinimide synthesis when the polyolefins and the maleic anhydride (MAH) are reacted under specific conditions more than one MAH is coupled to the polyolefin molecule or alternatively the so called olefin - MAH copolymers are formed. When the so formed intermediates having more than two carboxylic groups are reacted with amines, polyamines, alcohols, polyalcohols, alkanolamines or their mixtures of various compositions then higher molecular weight polyimide, polyamide, polyester, polyester-amide type end products are obtained (e.g. U.S. Patent No. 4.234,435).

Despite of their high DD effect, these ashless additives have only a low base number due to the blocking of their basic amino and imino groups and compared to the traditional succinimides they cause less damage to the fluor containing elastomer sealings of the engines.

Owing to the higher DD effect and significant viscosity and viscosity index increasing effect of these ashless additives they increase the performance level of the engine oils and proved also to be useful in replacing a part of the traditional additives used for improving flow properties reducing thereby the costs of motor oil production. In the published procedures various methods are recommended for the synthesis of the alkenyl-succinic anhydride type intermediates.

According to the US 4.234.435 and EP 0.208.560 patents the succinic anhydride (SA) : polyisobutylene (PIB $\overline{M}_n$ = 1300 - 5000) molar ratio can be increased over 1.05 by a one or multi step addition of the chlorine catalyst and by raising the temperature up to 160 - 220 °C. A serious disadvantage of this procedure is that hazardous chlorine is built in the polyolefin molecule during the addition reaction, and referred to the additive, it remains in the end product in a 0.001 - 0.5 weight percent.

Processes have also been reported where the polyisobutylene -MAH addition is achieved at high temperature (over 190 °C) without the use of a catalyst. SA/PIB molar coupling ratios higher than one have been achieved by using highly reactive (more than 70 percent alpha olefin content) polyisobutylene raw material and a large excess of MAH. The disadvantages of this method are the need for a more expensive raw material, the high reaction temperature and the long reaction time (e.g. European Patent No.0.271.937.).

A low temperature procedure has been reported in the PCT.No. WO 90/03359 where the polyisobutylene - maleic anhydride copolymer was prepared by using a radical initiator and an aromatic or chlorinated hydrocarbon solvent. In the PIB-MAH copolymer of alternating structure the average number of the PIB-MAH units varies from 1.1 to 20. When these type of intermediates are used for the acylation reaction then the end products might have a wide range of molar weight ($\overline{M}_n$ = 10 000 - 150 000).

According to the EP 0400866 and EP 0002286 European Patents maleic anhydride and other unsaturated comonomer or comonomers are grafted on the traditional viscosity index improving ethylene-propylene copolymers of a number average molecular weight higher than 10 000, preferably 100 000 - 200 000 by viscosity average molecular weight using chlorinated hydrocarbons or other solvents in the presence of a radical initiator.

The copolymer so prepared was then reacted with amines, polyamines etc. whereby a viscosity index improving additive with dispersant effect was obtained. For this purpose the use of polymers of number

average molecular weight below 30 000 as well as viscosity average molecular weight below 100 000 is considered to be disadvantageous by the above patents. According to the argument of these patents the hydrocarbon polymers of number average molecular weight below 30 000 were difficult to handle due to their unfavourable low temperature flow properties.

The methods published so far for the advantageous synthesis of the high molecular weight polyfunctional succinimides have both technological and structural limitations.

According to the advantageous examples patented for the synthesis of the polyisobutylene based succinimides the use of polyisobuthylens of average molecular weight $\overline{M}_n$ = 1300 - 2500 can be considered as typical and beneficial. As it is well known, the increasing of the average molecular weight of the polyisobutylene raw material above the limit of $\overline{M}_n$ = 2500 leads to considerable difficulties in the traditional technologies due to the high viscosity of the raw material. In addition to this, experience shows that due to the application of these raw materials a significant disadvantageous increase of the cold viscosity and a decrease of the polar nitrogen containing groups per unit mass of the additive and a concomitant decrease in the DD effect can be expected.

Succinimide derivatives obtained by grafting of ethylene - propylene copolymers have been produced and applied to achieve an additional DD effect beside their main viscosity and viscosity index increasing functions (EP 400866, EP 002286). For these kind of additives the optimal viscosity and viscosity index increasing effect occurs in the molecular weight range of $\overline{M}_n$ = 15000 - 200 000. Successful application of olefin copolymers of a number average molecular weight lower than 15 000 have not been reported probably due to a loss in their flow property improving effect.

Surprisingly, however, it has been recognised that by making use of our invention polyisobutylene based succinimide additives with significant DD, viscosity and viscosity index increasing properties can be synthesised even in the molecular weight range deemed unfavourable for both the polyisobutylene and the ethylene - propylene copolymers.

Our invention is based on the recognition that the mentioned drawbacks of the synthesis based on grafting the hydrocarbon polymers limiting the average molecular weight of the applicable raw material can be eliminated by the appropriate control of the grafting reaction. The recommended procedure makes feasible the synthesis of such intermediates from polyolefins of lower average molecular weight and in addition to this the intermediates obtained from polyisobutylenes or especially from their high alpha-olefin containing so called high reactivity homologous are suitable for the preparation of additives of new molecular structure showing higher viscosity and viscosity index improving effect, more advantageous antifriction effect and at the same time exhibit a better compatibility with the sealing materials as compared to the other well known ashless dispersants of molecular weight lower than 15 000.

The invention is related to an additive in a given case in an oil solution and the preparation thereof used in lubricating oils of internal combustion engines containing the imide - and/or ester and/or ester-amide derivative of the reaction product of a polyolefin, preferably polyisobutylene and some unsaturated reactive dicarboxylic acid and/or its anhydride, which comprises the reaction product of a polyolefin of a number average molecular weight 800 - 30 000, preferably 800 - 15 000 and an unsaturated reactive dicarboxylic acid and/or its anhydride, preferably maleic anhydride containing, on average, 1.6 - 6.0 SA-derivative per polyolefin chain and the concentration of molecules containing more than one SA - derivative is more than 25 weight percent in the additive, and the polyolefin is grafted or reacted with a more reactive, low molecular weight SA containing copolymer of low degree of polymerisation formed from a comonomer suitable for copolymerization containing olefinic double bond or from their mixture and from unsaturated reactive dicarboxylic acid and/or their anhydride, preferably maleic anhydride using the molar ratio 1.2 - 5.5 : 0.1 - 3.5 : 1 = MAH : comonomer : polyolefin, and the widening of the molecular weight distribution is less than 70 percent, referred to the starting polyolefin, while the SA groups of the grafted copolymer are reacted, in a 0.7 - 5.5 molar ratio, with compounds containing at least bifunctional amine and/or hydroxyl groups.

Further on, the invention is related to the preparation of an additive applicable to the above lubricating oil where the polyolefin, preferably polyisobutylene of an average molecular weight higher than 800 is reacted with unsaturated dicarboxylic acid and/or its anhydride, preferably maleic anhydride and with a more reactive, lower molecular weight comonomer with olefinic double bond susceptible to copolymerization or the mixtures of comonomers and/or with a copolymer of a low degree of polymerisation prepared previously consisting of unsaturated dicarboxylic acid and/or its anhydride and the comonomer and/or comonomers using the molar ratio 1.2 - 5.5 : 0.1 - 3.5 : 1 = maleic anhydride : comonomer : polyolefin, in a solvent or without a solvent preferably at a solvent concentration of 15 - 75 weight percent with respect to the reaction mixture, ensuring homogeneous phase, carried out in the presence of a radical initiator in 5 - 25 weight percent referred to the unsaturated dicarboxylic acid or its anhydride, at a pressure of 1 - $15*10^2$ kPa and in

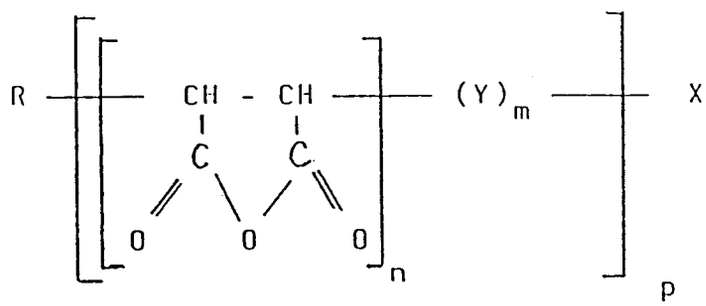
an inert and/or hydrocarbon atmosphere, at 80 - 180 °C, in 1 - 16 hours while the concentration of the unreacted dicarboxylic acid and/or anhydride and the comonomer and/or comonomers are kept below 5 weight percent; the obtained intermediate in which the increase of the number average molecular weight of the components measured by GPC is lower than 2.5 times of the molar weight of the starting polyolefin, the widening of the molar weight distribution is less than 70 percent referred to the starting polyolefin, is diluted with a base oil if desired and in the presence of a filtering aid is treated and filtered, and is reacted with compounds containing one or more at least bifunctional amine and/or hydroxyl groups, while the molar ratio of the compounds carrying the succinic anhydride groups and the amine and/or hydroxyl groups is 0.7 - 5.5 and the acylation is carried out in the presence or absence of a catalyst in 0.01 - 2 weight percent, at a pressure of 0.05 - 600 kPa, at 120 - 235 °C temperature, in 2 - 15 hours and the product, if desired, is modified in a usual way, diluted and filtered.

Further on, the scope of the invention covers also the intermediate used for the production of the additive and the preparation thereof. As polyolefins mostly homo and/or copolymers of alpha olefins such as ethylene, propylene, butene-1, isobutylene or other olefins and diolefins such as 1,3-butadiene are used with a number average molecular weight between 800 and 30 000, preferably in the range of 800 and 15000. Polyisobutylenes of a number average molecular weight between 1300 and 8000 were found to be the most advantageous.

Today, these kind of polyisobutylenes, especially of average molecular weight above 5000, have some limited applications as viscosity and viscosity index improving additives. Despite of their good thermal oxidation and shear stability their widespread application is limited because they increase the low temperature viscosity of the oils more than other type of viscosity index improving polymers. For this reason they cannot be applied alone in the production of modern multi-grade motor oils. The method applied in our invention dramatically decreases and in preferable cases eliminate these disadvantages of the PIB based viscosity index improving additives. Grafting the polar side chain into the PIB main chain results in a combined polymer structure having good thermal and chemical stability as well as viscosity increasing effect characteristic of polyisobutylenes, and at the same time the cold viscosity increasing effect is decreased significantly due to a decrease in the solubility of the polymer.

As comonomers reactive, polar and apolar monomers of low molecular weight such as ethylene, propylene, butene-1, 1,3-butadiene, isobutylene, C_{5-20} alpha olefins, styrene, acrylic acid, methacrylic acid, acrylates and methacrylates prepared from alcohols of C_{1-20}, acrylonitrile or their mixtures have been applied.

The polyolefin - polysuccinic acid derivatives prepared from polyolefin, preferably from polyisobutylene unsaturated dicarboxylic acid and/or its anhydride and from comonomer or from comonomer mixture having the general formula I. General formula (I).



where:

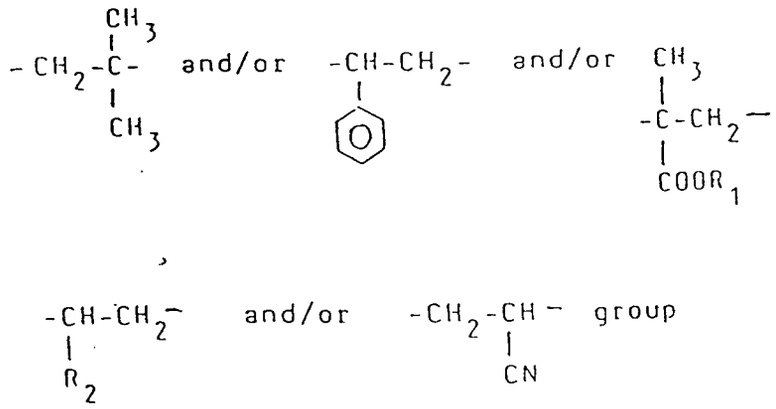
R is a polyolefin group, preferably polyisobutylene ($\overline{M}$ = 800 to 30 000, preferably 800 - 15 000),

n is an integer from 1 to 4, preferably 1,

m is an integer from 0 to 5, preferably 1,

p is an integer from 1 to 15, preferably from 2 to 6.

Y means:



and/or a group containing less than 30 carbon atoms, formed from an other olefin or diolefin or a mixture thereof,

X stands for hydrogen or a saturated or unsaturated group formed from Y group, and

R_1 and R_2 stand for hydrogen or C_{1-20} alkyl group.

Those derivatives are the most suitable where the number of the succinic anhydride (SA) groups linked to one polyolefin molecule is between 1.6 and 6 on average, preferably between 1.8 and 4 on average, and the concentration of the molecules containing more than one SA group is at least 25 weight percent, the concentration of the free maleic acid is less than 0.3 weight percent and the increase of the number average molecular weight of the components determined by GPC is smaller than 2.5 times the molar weight of the starting polyolefin. The intermediate consisting of the above long apolar polyolefin chain and a shorter, strongly polar, random or alternating copolymer chain is especially suitable for the preparation of the imide and/or ester and/or amide and/or ester-amide derivatives of great dispersing effect, where the derivatives occurring in one polyolefin chain could be identical or different.

It is also ensured by the multifunctional usually polar chain terminating groups that by using appropriate at least bifunctional basic reagents in the acylation reaction additives of chain like polymers are formed under advantageous conditions beside the usual crosslinked polymers.

The additive prepared according to this invention could contain components of various average molecular weight in which the average number of molecules linked by the carboxyl groups is between 2 and 100.

The additive prepared according to this invention exists advantageously in an oil solution. In this oil solution the concentration of the oil is at least 10 weight percent, preferably between 30 and 80 weight percent. For this purpose any type of refined oil, lubricating oil or base oil may be used.

In the actual preparation procedure maleic anhydride and comonomer or comonomers containing olefinic double bond or their copolymers are grafted to the starting polyolefins. During the reaction the double bonds of the maleic anhydride and the comonomer or the comonomers are activated by a radical initiator and due to the consecutive coupling to the polyolefins and /or due to the coupling of the random or alternating copolymers formed from the maleic anhydride and a comonomer a polymer chain is developed containing several SA groups (general formula I.).

The first step of the synthesis of the additive i.e. the reaction of the polyolefin and the unsaturated dicarboxylic acid and/or its anhydride, preferably maleic anhydride and comonomer or comonomers is performed in a homogeneous solution at an energetically favourable low temperature, with the suitable choice of the weight ratio corresponding to the molar ratio of the reactants of various reactivity, under circumstances unfavourable for the multiple coupling of the polyolefin, occasionally in the presence of compounds controlling the structure of side chain containing polar groups.

The reaction of the polyolefin and the unsaturated dicarboxylic acid and/or its anhydride preferably maleic anhydride and the comonomer or the comonomers was carried out in a solvent containing components also within the boiling range of 110 - 250 °C and in which the reactants and the intermediates were readily dissolved at a concentration of 20 - 75 weight percent, preferably 35 - 60 weight percent with respect to the reaction mixture, in the temperature range 80 - 180 °C, preferably between 120 - 160 °C, within a reaction period of 1 - 16 hours, using 1.2 - 5.5 : 0.1 - 3.5 : 1 maleic anhydride : comonomer : polyolefin molar ratio, and applying 5 - 25 weight percent peroxide, with respect to the amount of maleic anhydride, or other type of initiator such as azobisisobutyronitrile or cumene hydroperoxide or if desired, compounds or their mixtures controlling the incorporation ratios of the monomers in 0.01 - 5 weight percent, with respect to the amount of the maleic anhydride, at a pressure of 1 - 15×10^2 kPa, preferably at 1 - 5×10^2 kPa, in an inert

atmosphere such as nitrogen and/or hydrocarbon gas.

It has been found that high SA/polyolefin average molar ratio can be achieved, while the formation of the oil insoluble by-product is kept at a minimum level, if such a solvent or the mixture of solvents is used wherein the fraction of components having a boiling point below 250 °C is at least 3 weight percent. In order to decrease the concentration of by-products insoluble in oil the concentration of the comonomer or the comonomers should be less than 5 weight percent in the reaction mixture during the addition. These conditions can be met if the rates of addition of the MAH, the comonomer or the comonomers and the radical initiator decomposing in the temperature range 80 - 180 °C are set to appropriate values. For this purpose the radical initiator, the MAH as well as the comonomer or the comonomers are added in two or more portions or in a continuous way.

As initiator, organic peroxides, hydroperoxides or azo- compounds such as dibenzoyl peroxide, di-tert-butyl peroxide, azobis-isobutyro dinitrile, azodicarboxylic amide, or their mixture can be used.

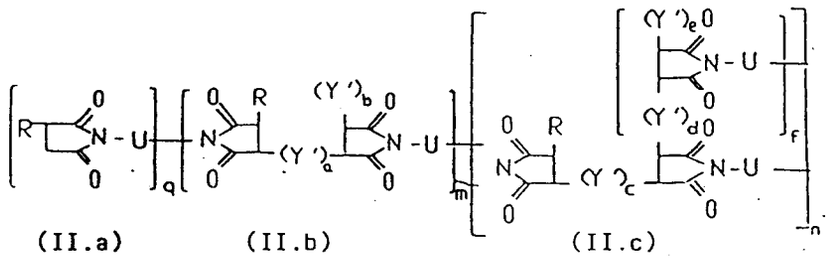
Compounds used for inhibiting undesirable side reactions, such as e.g. decarboxylation, resin formation, or for controlling the MAH : comonomer incorporation ratio could be carboxylic acids with 1 - 20 carbon number, dicarboxylic acids or anhydrides, hydroxycarboxylic acids, ketones, ethers, esters, alcohols, water or the mixtures of these and their derivatives. Isobutyl alcohol, isopropyl alcohol, succinic monobutyl ester can be applied advantageously. If desired, such additives are applied in a concentration of 0.01 - 5 weight percent with respect to the amount of the maleic anhydride. During the decomposition of these compounds or the radical initiators highly reactive species may be formed that may participate in the addition and polymerisation reactions occurring in the reaction mixture.

The reaction products have been identified by their ^{13}C and ^{1}H NMR spectra using deuterated chloroform as solvent. It has been pointed out that under the experimental circumstances applied in this invention the monomers added to the reaction mixture are mostly coupled to the α-double bond of the polyisobutylenes. This has been proved by the disappearance of the ^{13}C peaks at 114.5 and 143.6 ppm characteristic of the terminal double bonds of the polyisobutylenes, as well as the peaks of the ^{1}H spectra at 4.3 ppm and of the ^{13}C peaks at 136.6 ppm typical of the maleic anhydride and of the peaks characteristic of the double bonds of the comonomers. Experiments with maleic anhydride enriched in ^{13}C isotope proved the existence of bonds characteristic of the built in comonomer groups forming the grafted copolymer chains.

From the colourless - light brown intermediate prepared according to this invention the solvent can be recovered by stripping out the components of a boiling point below 250 °C and the remaining heavier part, if desired, can be diluted in 20 - 60 weight percent by refined oil, preferably by a refined oil having viscosity of 2 - 15 mm^2/s, at 100 °C.

The solution of the intermediate can be filtered without or with the addition of a filtration aid or filtration improving material in a 0.5 - 5 weight percent concentration.

If the intermediate prepared according to this invention is reacted in the second so called acylation step with polyamines, polyalcohols, alcanol amines containing at least two reactive groups and/or their mixtures and/or their derivatives by using hydrocarbon and/or refined oil as solvent at 120 - 235 °C, in inert e.g. nitrogen gas atmosphere at a pressure of 0.05 - $6x10^2$ kPa, in the presence of a catalyst in a 0.01 - 2 weight percent concentration then a polysuccinimide and/or polyamide and/or polyester and/or polyester-amide based mixture of the additive is obtained (such as the polysuccinimide, general formula II.) where one or more components can be formed with significantly different molecular weights depending on the reagents and molar ratios used. General formula II.



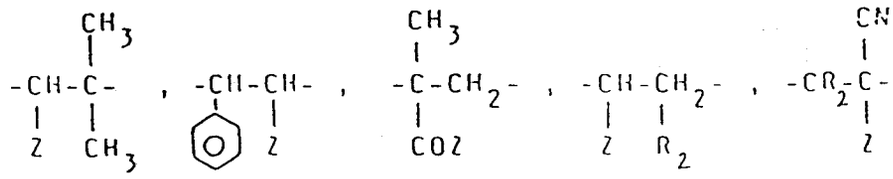
(II.a) (II.b) (II.c)

where:

R is a polyolefin, preferably polyisobutylene group (molar weight = 800 to 30 000, preferably 800 - 15 000),

U stands for an at least bifunctional group derived from polyalkylene - polyamines and/or polyalcohols and/or polyalkanolamines or other usual compounds containing basic nitrogen and/or hydroxyl group,

Y' means a:



group, or an other bifunctional group formed from an olefin or diolefin or a mixture thereof, or a monofunctional group obtained by transformation of the groups defined above,
Z means hydrogen or -NH-(CH_2CH_2NH)-H or -OR_1 group,
R_1 and R_2 stands for C_{1-20} alkyl group each,
a,b,c,d,e and f are integers from 0 to 5, preferably 1,
q,m,n are 0, 1 or an integer greater than 1, with the proviso that:
the sum of m and n is an integer greater than 1, the proportion of molecules containing groups (II.b) and/or (II.c) in the product is higher than 25 % by weight and the compounds of structures (II.a), (II.b) and (II.c) can be interconnected in an optional sequence.

The important feature of the additive prepared according to this invention is due to the new structure of the intermediate. In this intermediate the presumably reactive SA and other groups are closely located at the end of the long polyolefin chain. Consequently, the growing of the macromolecule by multiple or chain like coupling is not hindered sterically, as in the case of other intermediates where the SA groups are randomly located either at the end or in between the polyolefin chains.
As a multifunctional polyamine component e.g. ethylene- diamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, cyclic polyamine e.g. piperazine, diethyleneamino piperazine or the mixtures of these; as polyalcohol e.g. ethylene glycol, diethylene glycol, triethylene glycol, glycerol, trimethylolpropane or pentaerythritol; as amino-alcohol e.g. ethanolamine, diethanolamine, triethanolamine, or the mixtures and derivatives of these can be used.
Since in the additive the mole fraction of the various polymers of different molar weights can be altered in a wide range the need to prepare different motor oils is met easily by a slight modification of the preparation procedure.
According to our experience, especially those additive compositions proved to be advantageous where, in terms of weight percentage, the higher molar weight / lower molar weight ratio was in the 0.01 - 5 range.
The average molecular weight of the lower average molecular weight polymer is less than six times the number average molar weight of the polyolefin used as raw material. The experimental circumstances of the acylation have to be chosen in such a way that promote the formation of multiple couplings in the amide, imide and ester formation condensation reactions, i.e. that result in compounds characterised by polyamide, polyimide and polyester structure or by their combination. This can be achieved by keeping the molar ratio of the succinic anhydride group of the intermediate and the component to be acylated in the 0.7 - 5.5 : 1 range, preferably in the 1.7 - 4.5 : 1 range.
In order to ensure the required level of conversion in the acylation a 2 - 15 hour reaction period and, if desired, the usual acidic or basic catalysts were used in a 0.1 - 2 weight percent concentration range.
As a catalyst, acidic or basic compounds such as petroleum sulfonic acid, p-toluenesulfonic acid, sulfuric acid, potassium hydroxide, triethanolamine, ethanolamine or ion exchange resin, preferably in hydrogen ion form can be used in the acylation reaction.
In the polyester formation, which is one possible version of the acylation, the petroleum sulfonic acid can be used especially advantageously which so far has been suggested as a catalyst only in the preparation of low molecular weight ($\overline{M}_n$ < 3500) alkenyl succinic esters (Hungarian Patent No. 205.778).
After the acylation reaction the non-reacted acid can be removed, if this is needed. In order to promote other preferential by-effects such as the anticorrosion or anti-wear, antioxidant effect a structure modifying step can be applied as a finishing one. In this process a modifying compound is added in a 0.1 - 8 weight percent concentration referred to the reaction mixture, which is then stirred for 0.5 - 10 hours, at 80 - 230 °C temperature, in inert atmosphere.
For modification the usual modifying chemicals can be applied, such as sulfur, active sulfur containing compounds, phosphorus pentasulfide, boric acid or its derivative, zinc containing compounds like zinc dialkyldithiophosphate, copper compounds including organic copper salts or complexes, molybdenum

dioxide, organic acids e.g. fatty acids, glycolic acids, malic acid, fumaric acid, amides, alkenyl succinimide, their mixture or their derivatives.

After the completion of the acylation and the optional modifying reactions the volatile components can be stripped off from the reaction mixture in vacuum, at 160 - 210 °C, the reaction product is then diluted by refined oil, and if desired, it can be filtered without or with the use of filtration aids.

The various components of different average molecular weight of the end product exhibit characteristic differences, the additives containing the lower molecular weight components in a higher concentration have a higher acid neutralising capacity and deposition removing effect, whereas the products containing the higher molecular weight components in a higher concentration have a significant dispersion stabilising, viscosity and viscosity index increasing as well as an anti-wear effect.

In the products described herein the components are characterised by their number average molecular weight calculated as follows:

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

where

$\overline{M}_n$ is the number average molecular weight,

n_i is the mole number of the i-th polymer molecule,

M_i is the molar weight of the i-th polymer molecule,

i is 1,2,... positive integer.

The degree of polydispersity characterising the molecular weight distribution is the ratio of the weight average and number average molecular weights. The weight average molecular weight is calculated by the following equation:

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

where $\overline{M}_w$ is the weight average molecular weight, the other symbols have the same meaning as above. Polydispersity is calculated by the following equation:

$$\alpha = \frac{\overline{M}_w}{\overline{M}_n}$$

The widening of the molecular weight distribution ($\Delta\alpha$) is:

$$\Delta\alpha = \frac{\alpha - \alpha_{PIB}}{\alpha_{PIB}} \cdot 100$$

where α_{PIB} is the polydispersity of the polyolefin raw material and α is the polydispersity of the reaction product.

The invention is illustrated by the following non-limiting examples.

Example "A"

In a 3 dm^3 pressure proof, stirred tank reactor equipped with thermometer, inert gas supply and a cooler on the top connected to a condensate collecting vessel 1125 g (0.5 mole) polyisobutylene ($\overline{M}_n$ = 2250) and 1450 g xylene is weighed, the mixture is heated to 76 ± 4 °C in inert atmosphere and under stirring, 98.6 g

(1 mole) maleic anhydride, and at a rate of 0.7 g/h 2.8 g dibenzoyl peroxide are added and altogether 28 g isobutylene in four portions, 7 g each. After the completion of additions the reaction mixture is stirred for an hour under the above conditions. The xylene and other unreacted lighter components can be removed by distillation carried out at 140 °C, at 15 kPa pressure, for 1.5 hours. 1200 g refined lubricating oil (viscosity 3.5 mm^2/s at 100 °C, viscosity index 95, pour point -22 °C) is added to the intermediate. After homogenization at 135 - 150 °C and clarification the mixture is filtered in the presence of 3.5 weight percent filtration aid. The acid number of the yellow - brown, viscous, oily intermediate is 43.0 mg KOH/g, its maleic anhydride content is 1.5 mg/g and it contains 1.7 succinic anhydride group on the average referred to a PIB molecule. The SA/PIB succination ratio was calculated by the following equation:

$$SR = \frac{\overline{M}_{nPIB} \cdot E}{112.2 \cdot 10^3 - 98.6 \cdot E}$$

where

SR = SA/PIB succination ratio,

E = acid number of the intermediate (mg KOH/g),

$\overline{M}_{nPIB}$ = number average molar weight of the PIB.

Example "B"

The reaction vessel described in Example "A" is charged with 1125 g (0.5 mole) polyisobutylene of a number average molar weight $\overline{M}_n$ = 2250, 950 g SAE-30 base oil (viscosity 9.5 mm^2/s at 100 °C) and 110 g of MOL Rt. solvent of high aromatic content (having the trade name AROMATOL) and mixed. The mixture is stirred at atmospheric pressure in inert atmosphere, at 135 ± 6 °C and in 8 equal portions 118.3 g MAH, 76 g octylmethacrylate and 9.6 g di-tert-butyl peroxide are added to it in 4 hours. The reaction mixture is then stirred for further 6 hours and the AROMATOL and the other lighter components are boiled off at 155 °C, and 12 kPa pressure. To the intermediate 250 g SN-150/A (MOL Rt.) refined oil is added at 120 °C. The so obtained intermediate is first clarified with 2 weight percent filtration aid and in the presence of 1 weight percent of a filtration improving material it is filtered at 110 °C. The acid number of the diluted and filtered intermediate is 39.7 mg KOH/g, its maleic anhydride content is 2.8 mg/g and it contains 1.6 succinic anhydride group on average referred to a PIB molecule. The increase in the average molecular weight is less than 60 percent and the fraction of the compounds containing more than one succinic anhydride group per molecule is more than 55 percent.

Example "C"

Into the reaction vessel described in Example "A" 1200 g (0.15 mole) polyisobutylene ($\overline{M}_n$ = 8000), and 500 g xylene were weighted and mixed. The mixture was then heated to 115 °C and in six equal portions, in 3 hours 59.2 g (0.6 mole) maleic anhydride, 12.0 g azobisisobutyronitrile and 24.0 g styrene were added. Following the additions the reaction mixture was heated up to 180 °C and was stirred for a further 6 hours. The unreacted maleic anhydride was removed at 195 °C and 10 kPa pressure, the product was then mixed with 1150 g refined lubricating oil mentioned in Example "A" and the obtained mixture was filtered in the presence of 3 weight percent filtration aid. The acid number of the filtered and diluted intermediate is 23.9 mg KOH/g, its maleic anhydride content is 1.3 mg/g and it contains 3.3 succinic anhydride group, on average, referred to a PIB molecule. The increase in the average molecular weight and the widening of the molar weight distribution is less than 20 percent and the fraction of the compounds containing more than one SA group per molecule is 42 weight percent.

Example "D"

Into the reaction vessel described in Example "A" 1200 g (0.5 mole) polypropylene and a 9 : 1 weight ratio mixture of an SN 150/A base oil (commercial product of the MOL Rt.) and kerosine were added. The mixture was heated to 80 ± 4 °C and under stirring 98.6 g (1 mole) maleic anhydride and 4.2 g di-benzoyl peroxide were added, the mixture was stirred for 2 hours and the temperature was raised to 160 °C and the following components were added to it: 33 g isobutylene; as initiator 11.4 g di-tert-butyl peroxide; in 2 - 2 equal fractions per hour 43.3 g maleic anhydride, 6.5 g succinic monobutyl ester; 33 g styrene and within 6

hours in 5 equal fractions 88.7 g maleic anhydride.
The unreacted, lighter components were removed at 200 °C and at 10 kPa pressure during one and half hour. The product was then diluted with 1060 g of the base oil mentioned in Example "B" and the obtained mixture was filtered in the presence of 4 weight percent filtration aid, the acid number of the filtered and diluted intermediate was 60.1mg KOH/g, its maleic anhydride content was 2.1 mg/g, its average SA : PIB succination ratio was 2.4, the fraction of the components containing more than one SA group per molecule was 64 percent, the increase in the average molecular weight was less than 60 percent, and the measured widening of the molar weight distribution was 68 percent.

Example "E"

Into the reaction vessel described in Example "A" 0.08 mole polyisobutylene ($\overline{M}_n$ = 15000) 600 g xylene, 0.4 g cumene hydroperoxide and a 1 : 1 weight ratio mixture of fumaric acid : maleic anhydride mixture were added, the mixture was stirred and heated to 180 ± 5 °C, in inert atmosphere at 6 bar for 2.5 hours. The reaction mixture was then cooled down to 150 ± 4 °C and under stirring 9 g acrylic acid and 1.8 g di-tert-butyl peroxide as well as 12.8 g of the above acid mixture were added in 6 equal fractions in 6 hours in such a way that before each addition of the acrylic acid 0.5 - 0.5 g isobutyl alcohol was also added to the mixture.
After the distillation carried out for two hours at 165 °C and 15 kPa pressure, 1000 g oil characterised in Example "A", 2 - 2 percent filtration aid and filtration improving material were added and was filtered. The acid number of the filtered and diluted intermediate was 9.3 mg KOH/g, its maleic anhydride content was 1.7 percentage, its average dicarboxylic acid - polyisobutylene coupling ratio was 2.3, the fraction of the compounds containing more than one group originating from the dicarboxylic acid was 47 percent, the increase in the average molecular weight and in the widening of the molar weight distribution were less than 10 percent.

Example "F"

Into the reaction vessel described in Example "A" 500 g xylene saturated with water and 28.5 g isobutylene were weighed and under stirring the mixture was heated to 130 ± 5 °C in 2 hours, 0.75 mole (73.95 g) maleic anhydride and under continuous feed 14 g di-tert-butyl peroxide initiator was added, at 130 °C, to this reaction mixture 3 g succinic monobutyl ester were added in drops in half an hour, after about 0.25 hours 98.6 g maleic anhydride, 60 g styrene and 27 g di-tert-butyl peroxide initiator were added in 4-4, and the latter in 6 equal fractions. Before the addition of the last two fractions of the initiator 0.5 mole poly-isobutylene ($\overline{M}_n$ = 2250) and 0.5 mole (43.3 g) maleic anhydride were added to the reaction mixture which was then heated to 140 ± 5 °C and stirred for 1 hour. The unreacted, lighter components of the mixture were removed by boiling for 1.5 hours at 175 °C and at 15 kPa pressure. The product so obtained was then diluted with 1200 g of the base oil mentioned in Example "B" and was filtered in the presence of 2 weight percent filtration improving material. The saponification number of the filtered and diluted intermediate was 78.8 mg KOH/g, its maleic anhydride content was 1.9 mg KOH/g, its average SA : PIB succination ratio was 3.1, the increase of the average molecular weight was less than 30 percent, the widening of the molar weight distribution was 40 percent, the fraction of the components containing more than one succinic anhydride group per molecule was 65 percent.

Example " G "

Into the reaction vessel described in Example "A" 800 g SN 150/A base oil and 200 g xylene saturated with water were weighed and through this mixture 10 g " C_4 - fraction" (product of naphtha pyrolysis, commercial product of the TVK Rt.) was bubbled through and under stirring the mixture was heated to 90 ± 3 °C with a rate of 50 °C/hour and in 2 hours, 0.5 mole (49.3 g) maleic anhydride and 12 g dibenzoyl peroxide were added in 3 - 3 equal portions, the temperature of the reaction mixture was then raised to 140 ± 5 °C and in 4 hours 70 g styrene, 147.9 g (15 mole) maleic anhydride and 14 g di-tert-butyl peroxide were added in a continuous way. To the oily xylene solution of the low molecular weight copolymer 1125 g (0.5 mole) poly-isobutylene was added and the reaction mixture was then heated to 140 ± 5 °C and under continuous stirring for 1 hour 10 g di-tert-butyl peroxide was added, the mixture was then stirred for a further 1.5 hours.
The unreacted, lighter components of the mixture were removed by boiling as in Example "A" and the obtained intermediate diluted further by 300g SN 150/A oil was suitable for further use without filtering and

further processing. Its acid number was 72.4 mg KOH/g, maleic anhydride content was 1.8, its average SA : PIB succination ratio was 3.3, the increase of the average molecular weight was less than 35 percent, the widening of the molar weight distribution was 45 percent, the fraction of the components containing more than one succinic anhydride group per molecule was 73 percent.

Example " H " (Reference)

Into the reaction vessel described in Example "A" 1125 g (0.5 mole) polyisobutylene and 500 g xylene were weighed. The mixture was heated to 135 ± 5 °C , and in inert atmosphere, under stirring, in 5 equal fractions 111.0 g (1.1 mole) maleic anhydride and in 7 equal fractions 9 g di-tert-butyl peroxide initiator were added.
The lighter components of the mixture were removed as in Example " A " and the obtained intermediate was diluted by 1300 g of the oil mentioned in Example " B " , its acid number after clarification and filtration was 31.6 mg KOH/g, its free maleic anhydride content was 3.2 mg/g, the increase of its average molecular weight was less than 15 percent, the widening of the molar weight distribution was 45 percent, the average SA : PIB molar ratio was 1.3 the fraction of the components containing more than one succinic anhydride group per molecule was 35 percent.

Example " I "

Into the reaction vessel described in Example "A" 950 g (1 mole) polyisobutylene and under stirring in inert atmosphere at 180 ± 10 °C, 270 g of an isobutylene - styrene mixture (weight ratio 4 : 5), in 5 hours, in 5 equal fractions 246.5 g (2.5 mole) maleic anhydride and in 7 hours 28 g di-tert-butyl peroxide were added. After the first hour of the reaction but before all the maleic anhydride has been added 1 - 1 g of isopropyl alcohol was also added in drops to the reaction mixture. The lighter unreacted components of the mixture were removed as in Example " B " and the obtained intermediate was diluted by 1300 g of the base oil mentioned in Example " B ". Its acid number after clarification and filtration again according to Example " B " was 87.6 mg /g, its free maleic anhydride content was 3.0 mg/g, the average SA : PIB succination ratio was 1.5; the increase of its average molecular weight was 60 percent, the widening of the molar weight distribution was less than 68 percent, the fraction of the components containing more than one succinic anhydride group per molecule was 47 percent.

Example " J " (Reference)

Into the reaction vessel described in Example "A" 1300 g (1 mole) polyisobutylene and 350 g xylene were weighed and under stirring the mixture in inert atmosphere at atmospheric pressure it was heated to 145 °C and in 6 hours, 197.2 g (2 mole) maleic anhydride as well as 11.9 g cumene hydroperoxide and 6.8 g di-tert-butyl peroxide were added in 4 and 7 fractions. The unreacted, lighter components of the mixture were removed by boiling for 1 hour at 150 °C and at 15 kPa pressure. The mixture of the intermediate so obtained was then diluted with 1150 g of the oil mentioned in Example "A" and was filtered in the presence of 3 weight percent filtration improving material. The saponification number of the filtered and diluted intermediate was 70.3 mg KOH/g, its maleic anhydride content was 2.5 mg/g, its average number of the succinic anhydride groups linked to one PIB molecule was 1.6. The fraction of the components containing more than 3 succinic anhydride groups per molecule was 34 percent, the increase of the average molecular weight was 550 percent, the widening of the molar weight distribution was 85 percent referred to the polyisobutylene used as raw material.

Example " 1. "

In a stirred tank reactor equipped with reagent supply, condenser, sampling facility, nitrogen discharge vent, thermometer and pressure gauge 783.3 g of the acylation reagent described in example " A " is weighed at 65 °C and to this 14.2 g tetraethylenepentamine as well as 0.1 weight percent triethanolamine as catalyst were added. The reaction mixture was then heated to 175 - 180 °C, under stirring in inert atmosphere and the acylation reaction was then continued under such circumstances for 5 hours. This was followed by the addition of 3.1 g diethylenetriamine to the reaction mixture and at 190 °C, at 50, 30 and 10 kPa pressures the mixture was stirred for 1 - 1 hour. The nitrogen content of the end product was 0.8 percent, the ratio of the higher and lower molecular weight polymers was 0.6.

Example " 2. "

Into the stirred tank reactor described in Example " 1 " 84.7 g acylation reagent characterised in Example " B " and 5 g triethylenetetramine, 22.4 g triethanolamine were weighed at 60 °C . The reaction mixture was then heated to 175 - 180 °C, under stirring in inert atmosphere and the acylation reaction was then continued under such circumstances for 6 hours.
In the last four hours of the acylation reaction 300 kPa pressure was applied for 3 hours then for a further hour 10 kPa pressure. After filtration in the presence of 1 weight percent filtration aid the nitrogen content of the obtained product was 0.40 weight percent, the ratio of the higher and lower molecular weight polymers was 0.5.

Example " 3. "

Into the stirred tank reactor described in Example " 1 " 938.9 g of the intermediate according to Example " C " was weighed at room temperature then at 140 °C, 10.3 g diethylenetriamine was added to it. The acylation reaction was carried out under stirring in inert atmosphere at 50 kPa pressure for 4 hours while the temperature was raised to 190 °C at the rate of 20 °C/hour. After filtration at 120 °C in the presence of 1 weight percent filtration aid the nitrogen content of the obtained product was 0.4 weight percent, the ratio of the higher and lower molecular weight components was 2.3.

Example " 4. "

Into the stirred tank reactor described in Example " 1 " 746.8 g of the intermediate according to Example " D " , 0.2 weight percent malic acid catalyst and 12.3 g glycerol were added in two parts, at room and at 130 °C temperatures, then the acylation was carried out in inert atmosphere at 210 °C, at 400 kPa pressure for 4 hours, and at 10 kPa for 3.5 hours. The reaction mixture was then cooled down to 120 °C, and 3.1 g diethylenetriamine was added to it, then it was stirred at 155 °C, at 65 kPa pressure for 1 hour, then at 185 °C at 10 kPa pressure for 2 hours. After filtration in the presence of 1 weight percent filtration aid the nitrogen content of the obtained product was 0.11 weight percent, the ratio of the higher and lower molecular weight components was 0.2.

Example " 5. "

Into the stirred tank reactor described in Example " 1 " 844.5 g of the intermediate according to Example " E " was weighed. Under stirring in inert atmosphere, 1.24 g diethylenetriamine was added at room temperature then at 70 °C 2.27 g tetraethylenepentamine was added and the reaction was carried out for 2 hours at 130 °C. Then a further 0.6 g diethylenetriamine and 1.1 g of tetraethylenepentamine were added in drops to the reaction mixture. The reaction was carried out under atmospheric pressure for 4 hours at 190 °C, and was filtered at 120 °C in the presence of 1 weight percent filtration aid. The nitrogen content of the obtained product was 0.2 weight percent, the ratio of the higher and lower molecular weight components was 0.1.

Example " 6. "

Into the stirred tank reactor described in Example " 1 " 711.9 g of the intermediate according to Example " F " was weighed and in the presence of 0.2 weight percent petroleum-sulfonic acid catalyst, 6.0 g ethylenediamine was added to this mixture at room temperature and at atmospheric pressure, then the temperature was raised to 190 °C, and the pressure to $15x10^2$ kPa and the acylation reaction was carried out for 6 hours. To the reaction mixture 11.3 g tetraethylene- pentamine was added and at 215 °C, and 10^3 kPa pressure the reactants were mixed for 2 hours. After filtration at 120 °C in the presence of 1 weight percent filtration aid the nitrogen content of the obtained product was 0.9 weight percent, the ratio of the higher and lower molecular weight components was 1.25.

Example " 7. "

Into the stirred tank reactor described in Example " 1 " 774.9 g of the acylation reagent used in Example " G " was weighed, in inert atmosphere, at atmospheric pressure 8.76 g triethylenetetramine and under continuous stirring 9.49 g diethanolamine were weighed.

After the acylation reaction carried out at 175 °C under 50 kPa pressure for 4 hours 25 g monosuccinimide derivative (KOMAD-303, MOL Rt.) was added in drops at 120 °C, in 10 minutes. The reaction was continued for 3 hours at 170 °C and $2x10^2$ kPa and for a further 1.5 hour at 15 kPa pressure. The nitrogen content of the obtained product was 0.54 weight percent, the ratio of the higher and lower molecular weight polymers was 0.7.

Example " 8. " (Reference)

Into the stirred tank reactor described in Example " 1 " 711.3 g of the intermediate prepared according to Example "H" was weighed then in nitrogen atmosphere 10.3 g diethylenetriamine was added at room temperature and at 120 °C, 37.8 g tetraethylenepentamine was added and the acylation reaction carried out for 2 hours at 250 °C was followed by the addition of 13.6 g pentaerythritol and 2.4 g of petroleum sulfonic acid as catalyst. After a 3 hours final reaction period at 15 kPa pressure the product was filtered in the presence of 3 weight percent filtration aid. The difficult-to-filtrate product was only partially soluble in base oil due to its 2.2 percent nitrogen content.

Example " 9. "

Into the stirred tank reactor described in Example " 1 " 768.5 g of the acylation reagent used in Example " I " was weighed, in inert atmosphere, at atmospheric pressure. Under continuous stirring at 80 °C, first 21.2 g diethylene glycol was added in 0.5 hours using a 80 °C/hour heating rate, then 18.9 g tetraethylenepentamine was added in drops to the reaction mixture and the acylation reaction was carried out at 180 °C, under atmospheric pressure for 6 hours. The nitrogen content of the filtered end product was 0.82 weight percent, the ratio of the higher and lower molecular weight components was 0.4.

For the sake of easier handling and comparison - the oil content of all the end products was adjusted to 50 percent before further use. When the oil content of the end product prepared in the various examples was lower than 50 percent then it was adjusted to this value by dilution with the oil component used in the synthesis. For the dilutions refined lubricating oils characterised in Examples " A " and " B " were used.

By comparing the characteristics of the intermediates prepared in Examples " A " to " G " and " I " it turned out that under the circumstances applied in this invention the reaction between the comonomer(s), the polyolefin and the MAH leads to the linkage of copolymer chains containing 1.6 - 6, preferably 1.8 - 4 succinic anhydride groups on the average to the polyolefin molecule.

The efficiency of the detergent - dispersant effect of the additives mentioned in the above examples was evaluated according to the method described by L.Bartha et al.: Method of determination of optimum composition of detergent - dispersant engine oil additives, Hung. J. Ind. Chem.,1979 **7**, 359-366. The potential detergent - dispersant effect (PDDE) values are given in terms of percentage as the 225th part of the sum of the dispersion stabilising effect of the additive (detergent index, DI, %) and its washing effect (M, mm). The deposition reducing effect was evaluated by identical methods given in the above quoted publication on the basis of results obtained by the so called panel coking method. In addition to the above characteristics the dispersant effect of the additive has also been evaluated by the so called spot dispersancy test method. According to this method the oil mixture containing the additive or additives to be investigated is mixed in a high speed mixer with 2 percent carbon black of a specific quality and the suspension obtained is treated in six different ways (keeping them at various temperatures, in the presence or absence of water) and from the six suspensions samples are dropped on filter paper and the ratio of the diameters of the carbon black and the oil spots is evaluated after 48 hours. The theoretical maximum of the sum of the six results is 600 percent, the higher the dispersant effect the higher this value.

The detergent - dispersant effect of the products prepared in Examples 1 through 9 were evaluated in lubricating oils and are shown in Table 1.

Table 1

DD efficiency of additive compositions (3 weight percent in an SN-150 oil)	
Example No	PDDE, % * (100 max.)
Base oil	1
1.	96
2.	87
3.	76
4.	69
5.	74
6.	85
7.	87
8.	Cannot be evaluated
9.	86

* PDDE: potential detergent - dispersant effect

For these studies the products prepared according to the mentioned examples were mixed in 3 percent concentration into the base oil characterised by the following parameters:
Kinematic viscosity (100 °C): 5.2 mm^2/s
Viscosity index, VI_E : 101
The results of the detergent - dispersant effect studies of the oil compositions obtained using the products prepared in Examples 1.,2.,3.,7. and 8. as well as that of the reference are shown in Tables 2. and 3, while those on viscosity and VI improving are presented in Table 4.

Table 2.
DD properties of oil compositions

Oil compositions *	PDDE, % **	Deposition on the plate, mg
Additive according to:		
Example No.1.	94	3.2
Example No.2.	92	5.7
Example No.3.	85	10.4
Example No.7.	90	14.0
Reference additive (KOMAD - 301 ***)	81	9.0

* Components of the compositions

SAE-30 Base oil	91.0 %
Additives according to Examples No. 1.or 2.or 3.or 7.	4.0 %

Commercially available additives

Hyperbasic Ca-sulfonate 3.8 %

Zn-dialkyl-dithiophosphate 2.2 %

** PDDE: Potential detergent - dispersant effect

*** Commercially available KOMAD -301 ($\bar{M}_{nPIB}$ = 950; MOL Rt) 4.0 weight percent

Table 3.

DD efficiency studies of the additives by spot dispersancy test

Oil compositions	Spot dispersion, %
According to Example No.1.	420
According to Example No.7.	418
According to Example No.2.	412
According to Example No.3.	402
KOMAD-302*	428
Typical reference**:	
API SG/CD oil	411
Typical reference ***:	
API SF/CC oil	370

Dispersants were studied in the following SAE 10W-40 motor oil compositions:

Petroleum base oil: Variable, %

Pour point depressant: 1.0 %

PAO-6 (poly-alpha-olefin type synt. oil): 15.0 %

Polyisoprene VI improver: Variable, %

SG/CD performance level part package without dispersant: 6.4 %

Dispersant: 7.6 %

Total: 100 %

* Commercially available MOL Rt. product: traditional mono- bis succinimide type dispersant synthesised from polyisobutylene ($\bar{M}$=1000).

** Carrier Maximol 99 10W-40

*** Carrier MSF 15W-40

Table 4.

VI improving effect in oil compositions

Oil composition	Base oil* viscosity at 100 °C, mm²/s	Required VI improver, %
According to:		
Example No.1.	5.3	6.0
Example No.7.	5.4	6.5
Example No.2.	5.4	6.0
Example No.3.	5.8	5.0
KOMAD-302	5.4	8.0

Dispersants were studied in SAE 10W-40 oil compositions shown in Table 3. The viscosity of the compositions was set by the VI improver within the following limits:

Kinematic viscosity at 100 °C: 14.0-15.0 mm²/s

C.C.S. at -20 °C: 3100-3400 mPas

* Petroleum base oil and PAO-6 synthetic oil

Compatibility with sealing materials has been studied according to the Volkswagen test VW-3344 and the results are shown in Table 5.

Table 5

Data for the oil compositions obtained by the VW 3344 method			
Oil composition Additive according to:	Breaking load, mPa	Breaking elongation %	Storage at 100 % elongation
Example No.1	9.8	225	Crack free
Example No.7.	9.9	215	Crack free
Example No.2.	11.1	271	Crack free
Example No.3.	11.4	269	Crack free
KOMAD-302	7.3	136	Broken
Minimum level	8.0	160	Crack free

Dispersants were studied in the oil compositions shown in Table 3.

The structure and properties of the intermediates prepared according to Examples "A" through "G" and "I" and of the end products synthesised from these according to Examples 1. through 7. and 9. are similar to others prepared according to this invention and were also obtained under the advantageous experimental conditions and parameter combinations of the present invention.

The structure and properties of the intermediates and end products according to Examples "H" and "J" as well as 8., and also their preparation are different in some way from the advantageous structures and procedures of this invention.

The results concerning the detergent-dispersant, viscosity modifying, sealing compatibility studies of the end products obtained under advantageous acylation and modifying conditions according to the invention from the intermediates of advantageous structure and composition prepared according to the advantageous conditions of the invention are shown in Tables 1. through 5. and indicate that the efficiency of these products is either identical or superior as compared to the reference additives, i.e. their detergent - dispersant effect in the base oil either in themselves or in oil compositions is really advantageous. Their viscosity index improving effect and their compatibility with sealing materials are significantly superior as compared to commercially available reference additives. The use of additives prepared according to this invention further improves the properties of lubricants or fuels.

Due to their less significant cold viscosity increasing effect the applicable concentration can be further increased especially in the case of motor oils. Their preferential viscosity and viscosity index improving effect makes possible ta more extensive substitution of the traditional high molecular weight polymers. The feasibility of higher dosage level, of additives prepared according to the present invention starting from low molecular weight polyolefins, especially polyisobutylenes used so far for the preparation of ashless dispersants offers a more economic formulation of lubricants.

Claims

1. An additive, used in a given case in an oil solution in lubricating oils of internal combustion engines containing the imide- and/or ester and/or ester-amide derivatives of the reaction product of an unsaturated polyisobutylene and some unsaturated reactive dicarboxylic acids and/or their anhydride, which comprises the reaction product of a polyisobutylene of a number average molecular weight higher than 800 - 30 000 preferably 800 - 15 000 and an unsaturated reactive dicarboxylic acid and/or its anhydride, preferably maleic anhydride containing 1.6 - 6.0 SA - derivative per polyisobutylene chain on the average and in which the concentration of molecules containing more than one SA - derivative is more than 25 weight percent and the polyisobutylene is grafted or reacted with an SA containing copolymer formed from a more reactive, low molecular weight comonomer of a molecular weight less than 500, containing olefinic double bond or from a mixture of such comonomers and from unsaturated reactive dicarboxylic acid and/or their anhydride, preferably maleic anhydride using the molar ratio 1.2 - 5.5 : 0.1 - 3.5 : 1 = MAH : comonomer : polyisobutylene, and the widening of the molecular weight distribution is less than 70 percent, referred to the starting polyisobutylene, while the SA groups of the copolymer linked to the polyisobutylene are reacted, in a 0.7 - 5.5 ratio, with compounds containing at least bifunctional amine and/or hydroxyl groups.

2. The product according to Claim 1, wherein the dicarboxylic acid component of the copolymer grafted into the polyisobutylene chain is a succinic anhydride derivative.

3. The product according to Claim 1, wherein the dicarboxylic component of the copolymer grafted into the polyisobutylene chain contains on the average 1.8 - 4.0 succinic anhydride derivative.

4. The product according to Claim 1, wherein the copolymer grafted into the polyisobutylene chain contains identical or different succinic anhydride derivatives preferably imide, amide, ester, ester-amide and/or their mixtures.

5. The product according to Claim 1, wherein the concentration of the molecules containing more than one succinic anhydride derivative is more than 25 percent in the copolymer grafted into the polyisobutylene chain.

6. The product according to Claim 1, wherein the average number of molecules linked by the reaction of the carboxylic groups is between 2 and 100 in the components of various average molecular weight.

7. The process for preparing a detergent - dispersant additive or the preparation of its oil solution, wherein to the polyisobutylene of an average molecular weight 800 - 30000 maleic anhydride and comonomer with olefinic double bond or their copolymers are grafted by an addition reaction using the molar ratio 1.2 - 5.5 : 0.1 - 3.5 : 1 = maleic anhydride : comonomer : polyisobutylene, where the solvent concentration providing homogeneous phase is 10 - 75 weight percent, preferably 30 - 60 weight percent with respect to the reaction mixture, carried out in the presence of a radical initiator in 5 - 25 weight percent, and a monomer incorporation ratio controlling component in 0.01 - 5 weight percent referred to the maleic anhydride, at 1 - $15x10^2$ kPa pressure and preferably in nitrogen and/or hydrocarbon, atmosphere, at 80 - 180 °C, in 1 -16 hours while the concentration of the maleic anhydride and the comonomer is kept below 5 weight percent, the obtained intermediate is stripped off from its solvent content and is diluted with refined base oil, if desired, and when it is necessary it is clarified and filtered in the presence of filtration aid, the intermediate is reacted with compounds containing one or more at least bifunctional amine and/or hydroxyl groups, while the ratio of the compounds carrying the succinic anhydride groups and the amine and/or hydroxyl groups is 0.7 - 5.5 which is carried out in the presence of a catalyst in 0.1 - 2 weight percent referred to the reaction mixture at 0.015 - $6x10^2$ kPa pressure, at 120 - 235 °C temperature, in 2 - 15 hours and the product, if desired, is modified in a usual way, diluted and filtered.

8. The process according to Claim 7, wherein the reaction between the polyolefin, maleic anhydride and the comonomer is carried out in a solvent or in the mixture of solvents having hydrocarbon components of a boiling point less than 250 °C in a concentration of at least 3 weight percent.

9. The proces according to Claim 7, wherein the modification is carried out with compounds containing boron, sulfur, copper and/or molybdenum and/or polyalkenyl succinic anhydride or ester-amide.